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54 A method for the production of tenside alcohols and tenside alcohol ethers, the produced products and their use.

57 This document describes a method for the production of new tenside alcohols and tenside alcohol ethers by derivatizing olefins with between approximately 10 and 20 C-atoms or of mixtures of such olefins to form alkanols and possibly a subsequent alkoxylation, characterized by the fact that a C$_4$-olefin is subjected to a metathesis, the obtained olefins are dimerized and subsequently derivatized to form tenside alcohols and that they are possibly alkoxylated.

The olefin mixture obtained from the dimerization exhibits a high percentage content of branched components and less than 10% by weight of compounds that contain a vinyl idene group.

Also described here is the use of tenside alcohols and tenside alcohol ethers to form tensides by way of a glycosidation or poly-glycosidation, sulfation or phosphation.

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Description

This invention concerns a method for the production of tenside alcohols and tenside alcohol ethers that, among other uses, are very well suited as tensides or for the production of tensides. In that regard and based on C₄-olefin flows, olefins or olefin mixtures are produced through a metathesis and are dimerized to form an olefin mixture with between 10 and 16 C-atom that contains less than 10% by weight of compounds containing a vinyl idene group, the olefins are then derivatized to form tenside alcohols and these may then be alkoxylated.

Furthermore, the invention concerns the use of tenside alcohols and tenside alcohol ethers for the manufacture of tensides by way of a glycosidation or poly-glycosidation, sulfation or phosphation.

Fatty alcohols with chain lengths of between C_8 and C_{18} are used to produce non-ionic tensides. These are reacted with alkylene oxides to form the respective fatty alcohol ethoxylates (Chapter 2.3 in: Kosswig/Stache. "The Tensides", Carl Hanser Verlag, Munich, Vienna (1993). In that respect, the chain length of the fatty alcohol affects different properties of the tenside such as wetting power, foam formation, fat removal power, cleaning power.

Fatty alcohols with chain lengths of between C_8 and C_{18} can also be used to manufacture anionic tensides such as alkyl phosphates and alkyl ether phosphates. It is also possible to produce the respective sulfates in place of the phosphates (Chapter 2 in: Kosswig/Stache. "The Tensides", Carl Hanser Verlag, Munich, Vienna (1993).

Such fatty alcohols are available from natural sources such as fats and oils; they can also be produced synthetically from building blocks with a low number of carbon atoms. In that regard, the dimerization of an olefin to form a product with double the number of carbon atoms and its functionalization to form an alcohol represents one method. The reaction on a heterogeneous cobalt oxide / carbon catalyst can be run in that manner (DE-A-14 68 334), in the presence of acids such as sulfuric or phosphoric acid (FR 964 922, catalyzed with aluminum alkyl (WO 97/16398), or with a dissolved nickel complex catalyst (US-A-4 069 273). According to the information given in US-A-4 069 273, the use of this nickel complex catalyst and the use of 1,5-cyclo-octadiene or 1,1,1,5,5,5-hexafluoropentane-2,4-dione as complex former yields high-grade olefins that exhibit a high percentage content of dimerization products.

The olefin functionalization to form alcohols while building the carbon structure around a C-atom is appropriately achieved with a hydroformylation reaction that yields a mixture of aldehydes and alcohols that can then be hydrated to form alcohols. Approximately 7 million toms of this product are produced annually and worldwide with the hydroformylation of olefins. A summary of catalysts and reaction conditions for the hydroformylation process is given, for example, in Beller et al. in the Journal of Molecular Catalysis, A104 (1995), 17-85 and also in Ullmanns Encyclopedia of Industrial Chemistry, Vol. A5 (1986), page 217 and following, page 333, as well as in the related references.

It is known from WO 98/23566 that sulfates, alkoxylates, alkoxy sulfates and carboxylates of a mixture of branched alkanols (oxo-alcohols) have a good surface activity level in cold water and also have a good bio-degradability. The alkanols of the mixture used have a chain length of more than 8 carbon atoms and they exhibit on average of between 0.7 and 3 branchings. The alkanol mixture may be produced, for example, through a hydroformylation from mixtures of branched olefins that themselves may be obtained through a skeleton isomerization or through a dimerization of internal linear olefins.

The process has the advantage that the production of the dimerization feed does not require a C_3- or C_4-olefin flow. From this may be concluded that the olefins subjected to the dimerization must consist of ethylene according to the existing prior art (e.g., the SHOP process). Since ethylene is a relatively expensive base material for the tenside production, processes based on ethylene are economically less feasible than processes based on C_3- and/or C_4-flows.

A further disadvantage of these known methods consists in the fact that the production of branched tenside-oxo alcohols requires mixtures of internal olefins that are only available through an isomerization of alpha-olefins. Such methods always lead to isomer mixtures that are more difficult to manage than pure products with respect to processing, since the physical and chemical component data differ. Furthermore, there is the need to execute an additional process step, thus adding another disadvantage to the process.

The dimerization of a pure internal olefin such as 2-pentene or 3-hexene as well as the further derivatization of the dimerization products were not described previously.

The structure of the components found in the oxo-alcohol mixture is a function of the olefin mixture type that is subjected to the hydroformylation. Olefin mixtures that have been obtained through a skeleton isomerization from alpha-olefin mixtures lead to alkanols that are branched mainly at the ends of the main chain, i.e., in positions 2 and 3 calculated from the respective lobe ends (page 56, last section). From olefin mixtures obtained with the dimerization of olefins with a shorter chain length, one obtains oxo-alcohols using the method disclosed in this document, whose branchings are located closer to the center of the main chain, that is and as indicated in Table IV on page 68, very predominantly at C_4 and carbon atoms that are located further away in relation to the hydroxyl carbon atom. However and in relation to the hydroxyl carbon atom, fewer than 25% of the branchings are located at the C_2- and C_3-positions (pages 28/29 of this document).

From the alcohol mixtures, the surface-active end products are manufactured either by oxidizing the -CH_2OH-group to form a carboxyl group or by sulfating the alkanols or their alkoxylates.

Similar methods for the production of tensides are described in the PCT patent application WO 97/38957 and in the EP-A-787 704. An alpha-olefin is also dimerized in the method described there to form a mixture consisting mainly of vinyl-idene-branched olefin dimers (WO 97/38957).

/chemical formula/

The vinyl idene compounds are then isomerized in a double-link manner - and the

double-link thus migrates further to the center - and are then exposed to a hydroformylation to form an oxo-alcohol mixture. This is then reacted further to form tensides, e.g., by way of a sulfation. A grave disadvantage of this method consists in the fact that it is based on alpha-olefins. Alpha-olefins may be manufactured, for example, through an oligomerization of ethylene catalyzed on a transition metal, a Ziegler build-up reaction, wax-cracking or Fischer-Tropsch process, and are thus considered relatively expensive raw materials for the tenside manufacture. A further substantial disadvantage of this known process to produce tensides consists in the fact that a skeleton isomerization must be included between the dimerization of the alpha-olefins and the hydroformylation of the dimerization product, when one wishes to obtain mainly branched products. Based on the need to use a raw material that is relatively expensive for the tenside production and the need to include an additional process step, i.e., the isomerization, this known method becomes substantially disadvantageous with respect to economics.

In a surprising manner, it was now found that the production of branched olefins and alcohols (oxo-alcohols) that are easy to process further to form effective tensides - hereinafter called "tenside alcohols" - is not dependent on the use of alpha-olefins or olefins that are produced mainly from ethylene, i.e., it is possible to use cost-effective C_4-olefin flows and there is furthermore no need for the isomerization phase when one proceeds according to the method in accordance with the invention and described in the following.

C_4-olefin flows are mixtures that basically and in a preferred manner consist of 80-85% by volume and particularly preferred of more than 98% by volume of butene-1 and butene-2 and to a lesser extent - generally not more than 15 to 20% by volume - of n-butene and isobutene in addition to traces of C_5-hydrocarbons. These hydrocarbon mixtures - called Raffinate II in the technical terminology - occur as a secondary product during the cracking of high-molecular hydrocarbons such as crude oil. Although the low-molecular olefins, ethenes and propenes formed during these processes represent desirable raw materials for the production of polyethylene and poly-propylene and the hydrocarbon fractions are by way of C_6 used as fuels in combustion motors and for heating purposes, the raffinate II and particularly its C_6-olefins could so-far not been processed further and to a sufficient degree to produce valuable end products. Accordingly, the term C_4-olefin flows shall also include the gas mixture called raffinate II.

The method in accordance with the invention now opens a very favorable process path, i.e., the obtained C_4-olefin flows can be processed to form valuable tenside alcohols, from which can be manufactured non-ionic and anionic tensides using different and basically known processes.

An object of this invention consists in a method for the production of tenside alcohols and tenside alcohol ethers through a derivatization of olefins with approx. 10 to 20 C-atoms or of mixtures of such olefins and possibly a subsequent alkoxylation, characterized by the fact that one

a)   subjects a C_4-olefin mixture to a metathesis,

b)   separates olefins with between 5 and 8 C-atoms from the metathesis mixture,

c)   exposes the separated olefins individually or in a mixture to a dimerization to form olefin mixtures with between 10 and 16 C-atoms,

d)   exposes the obtained olefin mixture, possibly after a fractionation, to a derivatization to form a mixture of tenside alcohols, and

e)   possibly alkoxylates the tenside alcohols.

The basics for the metathesis used in process step a) are described, for example, in the Ullmanns Encyclopedia of Industrial Chemistry, 5th edition, volume A18, page 235/236. Further information to execute the method can be found, for example, in K.J. Ivin, "Olefin Metathesis, Academic Press, London, (1983); Houben-Weyl, E18, 1163-1223; R.L. Banks, Discovery and Development of Olefin Disproportionation, CHEMTEC (1986), February, 112-117.

In the presence of suitable catalysts and when using a metathesis for the main components butene-1 and butene-2 contained in the C_4-olefin flows, one obtains olefins with between 5 and 10 C-atoms, preferably with between 5 and 8 C-atoms, and one obtains particularly pentene-2 and hexene-3.

Suitable catalysts preferably consist of molybdenum compounds, tungsten compounds or rhenium compounds. It is particularly appropriate to perform the reaction in a heterogeneously catalyzed manner, in which case the catalytically effective metals are used particularly in connection with carriers made of Al_2O_3 or SiO_2. Examples of such catalysts are MoO_3 or WO_3 on SiO_2 or Re_2O_7 on Al_2O_3.

It is particularly favorable to run the metathesis in the presence of a rhenium catalyst, since this permits particularly mild reaction conditions. In this case, the metathesis can be performed at a temperature of between 0 and 50 °C and at low pressures of between 0.1 and 0.2 MPa.

With the dimerization of the olefins or olefin mixtures obtained in the metathesis process step, one obtains dimerization products that - in view of the further processing to form tenside alcohols - exhibit particularly favorable components and particularly favorable compositions, when

one uses a dimerization catalyst that contains at least one element of the secondary group VIII in the periodic system for elements,

and one selects the catalyst composition and the reaction conditions in such a manner that one obtains a dimer mixture containing less than 10% by weight of compounds that have a structural element of the formula 1

(vinyl idene group)

/formula/

where A^1 and A^2 are aliphatic hydrocarbon rests.

In a preferred manner, the internal linear pentenes and hexenes contained in the metathesis products are used for the dimerization. Particular preference is given to the use of 3-hexene.

The dimerization can be performed in a homogeneously or heterogeneously catalyzed manner. Preference is hereby given to the heterogenous process, since this simplifies the catalyst separation and the method thus becomes more economical and no sewage water that damages the environment is produced, i.e., unlike the sewage water generally produced when separating dissolved catalysts with a hydrolysis, for example. A further advantage of the heterogeneous method consists in the fact that the dimerization product contains no halogens, particularly no chlorine or fluorine. Homogeneously dissolving catalysts generally contain ligands with halogenide or they are used in combination with halogen-containing co-catalysts. From such catalyst systems, halogen can be introduced into the dimerization products and this has a substantially negative effect on the product quality as well as the further processing and particularly the hydroformylation to form tenside alcohols.

The heterogeneous catalysis is appropriately performed with combinations of oxides of metals from the secondary group VIII with aluminum oxide on carrier materials consisting of silicon oxides and titanium oxides like those known from DE-A-43 39 713. The heterogeneous catalyst can be used on a solid bed - and then in a large-grained form as a 1 mm to 1.5 mm grit - or suspended (particle size between 0.05 and 0.5 mm). In the heterogeneous form, the dimerization is run appropriately in a closed system at temperatures of between 80 and 200 °C, preferably at between 100 and 180 °C, and under the pressure occurring at the reaction pressure and possibly under a protective gas overpressure. To achieve optimal reaction rates, a reaction mixture is circulated several times, in which case a certain percentage content of the circulated product is removed and replaced with the raw material.

In the dimerization in accordance with the invention, one obtains mixtures of simple unsaturated hydrocarbons, most of whose components exhibit a chain length that is twice as long as that of the initial olefins.

The dimerization catalysts and the reaction conditions are selected appropriately within the scope of the above information in such a manner that at least 80% of the dimerization mixture components have one or two branchings on adjacent C-atoms at a range of between 1/4 and 3/4 and preferably of between 1/3 and 2/3 of the chain length of their main chain.

Their very high percentage content - generally more than 75% and particularly more than 80% - of components with branchings and the low percentage content - generally less than 25% and particularly less than 20% - of linear olefins is very characteristic for the olefin mixtures prepared in accordance with the invention. Another characteristic consists in the fact that mainly groups with (y-4) and (y-5) C-atoms are linked at the branching points of the main chain, in which case "y" represents the number of carbon atoms of the monomers used for the dimerization. The value (y-5) indicates that there is no lateral chain.

For C_{12}-olefin mixtures produced in accordance with the invention, the main chain preferably carries methyl or ethyl groups at the branching points. The position of the methyl and ethyl groups on the main chain is also characteristic: In a mono-substitution, the methyl or ethyl groups are in the position $P = (n/2)-m$ of the main chain, in which case n equals the length of the main chain and m is the carbon number of the lateral groups; in di-substitution products, one

substituent is in the position P and the other on the adjacent C-atom P+1. The percentage contents of mono-substitution products (simple branching) in the olefin mixture produced in accordance with the invention characteristically vary between 40 and 75% by weight, while the percentage contents of double-branched components vary between 5 and 25% by weight.

It was also determined that the dimerization mixtures are particularly easy to derivatize further when the position of the double-link meets certain requirements. In these advantageous olefin mixtures, the position of the double-links in relation to the branchings is characterized by the fact that the ratio between the "aliphatic" hydrogen atoms and the "olefinic" hydrogen atoms varies as follows:

$$H_{aliphatic} : H_{olefinic} = (2 \times n-0.5) : 0.5 \text{ to } (2 \times n-1.9) : 1.9,$$

where n represents the carbon atom number of the olefin obtained with the dimerization. ("Aliphatic" hydrogen atoms are considered those linked to carbon atoms that do not participate at any C=C double-link (Pi link), while "olefinic" hydrogen atoms are considered those linked to a carbon atom that activates a Pi-link. Particularly preferred are dimerization mixtures with the following ratio

$$H_{aliphatic} : H_{olefinic} = (2 \times n-1.0) : 1 \text{ to } (2 \times n-1.6) : 1.6.$$

The new olefin mixtures that are obtained with the method in accordance with the invention and exhibit the above-mentioned structure are also an object of this invention. They are valuable intermediate products, particularly for the production of branched primary alcohols and tensides that is described later; they can also be used in other industrial processes that are based on olefins, particularly in the case the end products are expected to exhibit an improved biodegradability.

When the olefin mixtures in accordance with the invention are used for the production of tensides, they are initially and in a known manner derivatized to form tenside alcohols.

This can be achieved in different ways, including the direct or indirect addition of water (hydration) on the double-link or an addition of CO and hydrogen (hydroformylation) on the C=C=double-link.

The hydration of the olefins obtained with process step c) is generally achieved with a direct addition of water under a proton catalysis. It is only natural that this can be achieved as well in an indirect manner such as the addition of a high-percentage sulfuric acid to an alkanol sulfate and a subsequent saponification to form an alkanol. The more appropriate water addition is performed in the presence of acid - particularly heterogeneous - catalysts and generally at the highest-possible partial olefin pressure and at the lowest-possible temperatures. Particularly phosphoric acid on carriers such as SiO_2 or celite and also ion exchangers have proven themselves as catalysts. Selecting the conditions is a function of the reactivity of the olefins to be reacted and can be determined routinely with initial tests (Reference: e.g., A.J. Kresge et al. J.Am.Chem.Soc. 93, 4907 (1971); Houben-Weyl, Vol. 5/4(1960), pages 102-132 and 535-539). The hydration generally leads to mixtures of primary and secondary alcohols in which there are more secondary
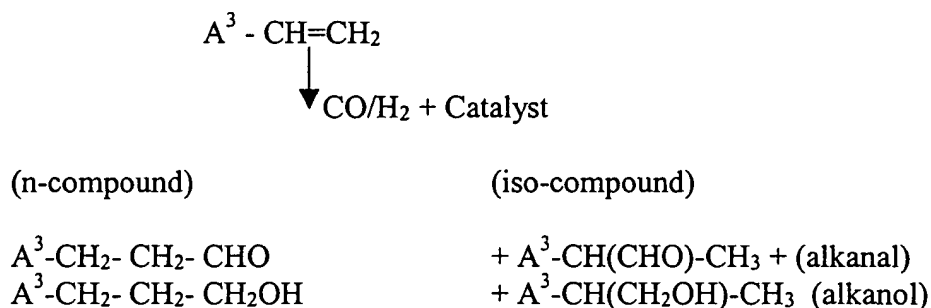
alkanols.

The tenside production on the basis of primary alkanols is more favorable. Accordingly, it is preferred to derivatize the olefin mixtures obtained in step c) by a reaction with carbon monoxide and hydrogen in the presence of suitable catalysts that preferably contain cobalt or rhenium and to hydroformylate them to form branched primary alcohols.

Accordingly, a further preferred object of this invention consists in a method for the production of mixtures of primary alkanols that are suitable for a further processing to form tensides by way of a hydroformylation of olefins and the method is characterized by the fact that the above-described olefin mixtures in accordance with the invention are used as the initial material.

A good overview for the hydroformylation method with numerous further references is found, for example, in the extensive paper written by Beller et al. in the Journal of Molecular Catalysis, A104 (1995), 17-85, or in Ullmanns Encyclopedia of Industrial Chemistry, Vol. A5 (1986), page 217 and following, page 333, as well as in the related references.

The extensive information given there permits the expert to also hydroformylate the branched olefins in accordance with the invention. In this reaction, CO and hydrogen are deposited on olefinic double-links, in which case are obtained mixtures of aldehydes and alkanols according to the following reaction formula:

$$A^3 - CH{=}CH_2$$

$$\downarrow CO/H_2 + \text{Catalyst}$$

(n-compound)   (iso-compound)

$A^3\text{-}CH_2\text{-} CH_2\text{-} CHO$ $+ A^3\text{-}CH(CHO)\text{-}CH_3 + $ (alkanal)
$A^3\text{-}CH_2\text{-} CH_2\text{-} CH_2OH$ $+ A^3\text{-}CH(CH_2OH)\text{-}CH_3$ (alkanol)

(A^3 = hydrocarbon rest)

The mol ratio between n- and iso-compounds in the reaction mixture is a function of the selected process conditions for the hydroformylation and of the catalyst to be used and generally varies between 1:1 and 20:1. The hydroformylation is generally performed at a temperature range of between 90 and 200 °C and at a CO/H_2 pressure of between 2.5 and 35 MPa (25 to 350 bar). The mixture ratio between carbon monoxide and hydrogen is a function of the preferred product to be produced, i.e., alkanals or alkanols. The appropriate range $CO{:}H_2$ varies between 10:1 and 1:10 and preferably between 3:1 and 1:3, in which case one selects the range of the lower partial hydrogen pressure for the production of alkanals and the range of the higher partial hydrogen pressure such as $CO{:}H_2 = 1{:}2$ for the production of alkanols.

Particularly suited catalysts consist of metal compounds of the general formula $HM(CO)_4$ or $M_2(CO)_8$, in which case M is a metal atom, preferably a cobalt, rhodium or ruthenium atom.

From the respective catalysts or initial catalyst stages used for the process, catalytically active species of the general formula $H_xM_y(CO)_zL_q$ are generally formed under hydroformylation conditions, in which case M stands for a metal of secondary group VIII, L for a ligand that can be a phosphine, phosphite, amine, pyridine or any other donor compound - also in a polymer form - and q, x, y and z are whole numbers as a function of the metal valence and type as well as of the ligand's linking power, in which case q can also be 0.

Metal M preferably consists of cobalt, ruthenium, rhodium, palladium, osmium or iridium or particularly preferred of cobalt, rhodium or ruthenium.

Suitable rhodium compounds or complexes consist, for example, of rhodium(II) and rhodium(III) salts such as rhodium(III) chloride, rhodium(III) nitrate, rhodium(III) sulfate, potassium rhodium sulfate, rhodium(II) or rhodium(III) carboxylate, rhodium(II) and rhodium(III) acetate, rhodium(III) oxide, salts of the rhodium(III) acid such as tris-ammonium hexachloro-rhodate-(III). Also suited are rhodium complexes such as rhodium bis-carbonyl acetyl acetonate, acetyl-acetonato bis-ethylene rhodium(I). Preference is given to rhodium bis-carbonyl acetyl acetonate or rhodium acetate.

Suitable cobalt compounds consist, for example, of cobalt(II) chloride, cobalt(II) sulfate, cobalt(II) carbonate, cobalt(II) nitrate, their amine or hydrate complexes, cobalt carboxylates such as cobalt acetate, cobalt ethyl hexanoate, cobalt naphthanoate as well as the cobalt caprolactamate complex. Carbonyl complexes of the cobalt such as di-cobalt carbonyl, tetra-cobalt dodecacarbonyl and hexacobalt hexadecacarbonyl can be used as well.

The compounds of cobalt, rhodium and ruthenium mentioned here are basically known and are sufficiently described in the available references or they can be prepared by the expert in a similar manner than the already known compounds.

The hydroformylation can be performed by adding inert solvents or dilution agents or without adding such agents. Suitable inert additives consist, for example, of acetone, methyl ethyl ketone, cyclo-hexanone, toluene, xylene, chlorobenzene, methylene chloride, hexane, petroleum ether, acetonitrile as well as the high-boiling percentage contents from the hydroformylation of the dimerization products.

When the aldehyde content in the obtained hydroformylation product is too high, this situation can be remedied in a simple manner with a hydration with hydrogen, for example, in the presence of Raney nickel or with the use of other catalysts that are known for hydration reactions and contain particularly copper, zinc, cobalt, nickel, molybdenum, zircon or titanium. In that regard, most of the aldehyde percentage content will have been hydrated to alkanols. A practically complete removal of the aldehyde content from the reaction mixture can be achieved, if desired, with a post-hydration under particularly careful and economical conditions with an alkali borhydride.

The mixtures of branched primary alkanols that can be obtained with the hydroformylation of the olefin mixtures in accordance with the invention also form an object of this invention.

Non-ionic or anionic tensides can be produced in different ways from the alkanols in accordance with the invention. Non-ionic tensides are obtained by reacting the alkanols with alkylene oxides (alkoxylation) of the formula II

/formula/   (II)

where R^1 is hydrogen or a linear or branched aliphatic rest of the formula C_nH_{2n+1} and n represents a number of between 1 and 16 and preferably of between 1 and 8. R^1 stands in particular for hydrogen, methyl or ethyl.

The alkanols in accordance with the invention can be reacted with one single alkylene oxide species or with several different ones. The alkanol reaction with the alkylene oxides forms compounds that again carry an OH-group and thus can react again with an alkaline oxide molecule. Accordingly and as a function of the mol ratio between alkanol and alkylene oxide, one obtains reaction products that have more or less long polyether chains. The polyether chains may contain between 1 and approx. 200 alkylene oxide modules. Compounds, whose polyether chains contain between 1 and 10 alkylene oxide modules, are preferred.

The chains may consist of the same chain links or they may have different alkylene modules that differ from each other with respect to their rest R^1. These different modules may be present within the chain in a statistical distribution or in the form of blocks.

The following reaction formula shall explain the alkoxylation of the alkanols in accordance with the invention with the example of a reaction with two different alkylene oxides that are used in two different mol quantities x and y.

/reaction formula/

R^1 and R^{1a} are different rests within the scope of the definition given above for R^1, and R^2-OH is a branched alkanol in accordance with the invention.

The alkoxylation is preferably catalyzed with strong bases that are generally added in the form of alkali hydroxides or earth alkali hydroxides, generally at a quantity of between 0.1 and 1% by weight in relation to the alkanol R^2-OH. (See G. Gee et al., J.Chem.Soc. (1961), page 1345; B. Wojtech, Makromol. Chem. 66, (1966), page 180).

An acid catalysis of the addition reaction is also possible. In addition to Bronsted acids, it is also possible to use Lewis acids such as $AlCl_3$ or BF_3. (See P.H. Plesch, The Chemistry of Cationic Polymerization, Pergamon Press, New York (1963).

The addition reaction is run in a closed container at temperatures of between approx. 120 and 220 °C and preferably of between 140 and 160 °C. Alkylene oxide or the mixture of different

alkylene oxides is supplied to the mixture consisting of the alkanol mixture in accordance with the invention and alkali at the steam pressure of the alkylene oxide mixture that occurs at the selected reaction temperature. If desired, the alkylene oxide can be diluted with an inert gas to between approx. 30 and 60%. This provides an additional safety against an explosion-like poly-addition of the alkylene oxide. The use of an alkylene oxide mixture yields the formation of polyether chains, in which the different alkylene oxide modules are distributed in a practically statistical manner. Variations in the module distribution along the polyether chain occur on the basis of different component reaction velocities and can be achieved by continuously adding an alkylene oxide mixture with a program-controlled composition. When the different alkylene oxides are brought to react one after the other, one obtains polyether chains with a block-like distribution of the alkylene oxide modules.

The polyether chain length within the reaction product varies statistically around a mean value that basically corresponds to the stoichiometric value obtained from the composition.

The alkoxylates based on the olefin mixtures and alkanol mixtures in accordance with the invention also form an object of this invention. They have a very good surface activity level and can thus be used in many applications as neutral tensides.

Based on the alkanol mixtures in accordance with the invention, it is also possible to produce surface-active glycosides and poly-glycosides (oligo-glycosides). These substances also exhibit very good tenside properties. They are obtained with a single o multiple reaction (glycosidation or poly-glycosidation) of the alkanol mixtures in accordance with the invention with mono-, di- or poly-saccharides with the exclusion of water under an acid catalysis. Examples of suitable acids are HCl or H_2SO_4. Oligo-glycosides with a statistical chain length distribution are generally obtained, in which case the average degree of oligomerization varies between 1 and 3 saccharide rests.

In another standard synthesis, the saccharide is first and under an acid catalysis acetalized with a low-molecular alkanol such as butanol to form butanol glycoside. This reaction an also be performed with aqueous solutions of the saccharide. The lower alkanol glycoside such as butanol glycoside is then reacted with the alkanol mixtures in accordance with the invention to form the desired glycosides in accordance with the invention. After neutralizing the acid catalysts from the equilibrium mixture, e.g., by way of a distillation in a vacuum, it will be possible to remove excess alkanols with long and short chains.

A further standard method runs by way of the O-acetyl compounds of the saccharides. With the help of halogen hydrogen that was preferably dissolved in acetic acid, these are converted into the corresponding O-acetyl halosaccharides that react in the presence of agents that link acids with the alkanols to form the acetylized glycosides.

The glycosidation of the alcohol mixtures in accordance with the invention is preferably carried-out with mono-saccharides, i.e., hexoses such as glucose, fructose, galactose, mannose as well as the pentoses such as arabinose, xylose or ribose. Glucose is particularly preferred for the glycosidation of the alkanol mixtures in accordance with the invention. It is only natural that mixtures of the above-mentioned saccharides can be used for the glycosidation. In this case, one

obtains glycosides with statistically distributed sugar rests as a function of the reaction conditions. The glycosidation can also be performed several times and poly-glycoside chains will then be deposited on the hydroxyl groups of the alkanols. With a poly-glycosidation and the use of several saccharides, the saccharide modules may be distributed statistically within the chain or may form blocks of the same modules.

One may obtain furanose or pyranose structures as a function of the selected reaction temperature. The reaction can also be performed in suitable solvent or diluting agents to improve the solubility ratios.

Standard methods and suitable reaction conditions have been described in several publications such as in "Ullmanns Encyclopedia of Industrial Chemistry", 5th edition, Vol. A25 (1994), pages 792-793 and in the references listed there, by K. Igarashi, Adv. Carbohydr.Chem.Biochem. 34, (1977), page 243-283, by Wulff and Röhle, Angew.Chem. 86 (Applied Chem. 86), (1974), page 173-187 or by Krauch and Kunz, Reactions of the Organic Chemistry, page 405-408, Hüthig, Heidelberg, (1976).

Glycosides and poly-glycosides (oligo-glycosides) that can be produced on the basis of olefin mixtures and alkanol mixtures in accordance with the invention also form an object of this invention.

The alkanol mixtures in accordance with the invention as well as the polyethers produced from them can be converted into anionic tensides by esterifying (sulfating) them in a generally known manner with sulfuric acid or sulfuric acid derivatives to form alkyl sulfates or alkyl ether sulfates or with phosphoric acid or its derivatives to form acid alkyl phosphates or alkyl ether phosphates.

Sulfation reactions for alcohols have been described already, e.g., in US-A-3 462 525, 3 420 875 or 3 524 864. Details on the reaction execution are found in "Ullmanns Encyclopedia of Industrial Chemistry", 5th edition, Volume A25, (1994), page 779-783 and in the references listed there.

When sulfuric acid itself is used for the esterification, it is appropriate to use between 75 and 100% by weight and preferably between 85 and 98% by weight acid (so-called "concentrated sulfuric acid" or "monohydrate"). The esterification can be performed in a solvent or diluting agent, when this is desirable to control the reaction, e.g., the heat development. The alcoholic reactant is generally provided first and the sulfation agent is added slowly under a continuous stirring. When one desires a complete esterification of the alcohol component, one uses the sulfation agent and the alkanol at a mol ratio of between 1:1 and 1:1.5 and preferably of between 1:1 and 1:1.2. Smaller quantities of the sulfation agent may be desirable, when mixtures from alkanol alkoxylates in accordance with the invention are to be used and combinations of neutral and anionic tensides are to be produced. The esterification is generally performed at temperatures of between room temperature and 85 °C and preferably of between 45 and 75 °C.

It may be appropriate to perform the esterification at the boiling point of and in a low-boiling solvent and diluting agent that does not mix with water, in which case water formed during the esterification shall be distilled-off in an azeotropic manner.

Instead of using sulfuric acid of the above-mentioned concentration, the sulfation of the alkanol mixtures in accordance with the invention can also be performed with sulfur trioxide, sulfur trioxide complexes, solutions of sulfur trioxide in sulfuric acid ("Oleum"), chlorosulfonic acid, sulfuryl chloride or also amidosulfonic acid. The reaction conditions shall then be adjusted accordingly.

When sulfur trioxide is used as the sulfation agent, the reaction can be performed in an advantageous manner in a falling film reactor in a counterflow, possibly also continuously.

The quantities are neutralized after the esterification by adding alkali and are processed possibly after removing excess alkali sulfates and possibly existing solvents.

The acid alkanol sulfates and alkanol ether sulfates obtained after sulfating alkanols and alkanol ethers in accordance with the invention and their mixtures and their salts are also the object of this invention.

In an analogous manner, alkanols and alkanol ethers in accordance with the invention and their mixtures can be reacted with phosphation agents to also form acid phosphoric acids (phosphated). Suitable phosphation agents are phosphoric acid, poly-phosphoric acid and phosphorus pentoxide as well as $POCL_3$, when this is followed by a hydrolysis of the remaining acid chloride function. The alcohol phosphation is described, for example, in Synthesis 1985, pages 449 to 488.

The acid alkanol phosphates and alkanol ether phosphates obtained with the phosphation of alkanols and alkanol ethers in accordance with the invention and their mixtures are also an object of this invention.

Finally, the use of alkanol ether mixtures, alkanol glycosides as well as the acid sulfates and phosphates of the alkanol mixtures and the alkanol ether mixtures that can be produced with the olefin mixtures in accordance with the invention as tensides are an object of the invention.

The following examples explain the production and use of the tensides in accordance with the invention.

Example 1

Production of C_5/C_6-olefins from C_4-olefin flows through a metathesis

A C_4-fraction that was free of butadiene, had a total butene content of 84.2% by weight and a mol ratio 1-butene : 2-butene of 1.06 ("Raffinate II") was passed continuously through a tube reactor filled with a heterogenous Re_2O_7/Al_2O_7 contact at 40 °C and 10 bar. The catalyst feed was set to 4,500 kg/(m^2·h). The reaction discharge was separated by distillation and contained the following (data in percent by mass):

Ethene: 1.15%, propene: 18.9%, butane: 15.8%, 2-butene: 19.7%, 1-butene: 13.3%, i-butene: 1.00%, 2-pentene: 19.4%, methyl butene: 0.45%, 3-hexene: 10.3%.

Examples 2A and 2B

Heterogeneously catalyzed dimerization of 3-hexene

2A. Solid bed method

A reactor that has a diameter of 16 mm and can be heated in an isothermal manner was filled with 100 ml of a catalyst with the composition indicated below:

50% by weight NiO, 34% by weight SiO_2, 13% by weight TiO_2, 3% by weight Al_2O_3 (according to DE-A-43 39 713), then conditioned for 24 hours in N_2 at 160 °C and used as a grit of between 1 and 1.5 mm.

The number of tests was 5, in which case 3-hexene (99.9% by weight, 0.1% by weight C_7 to C_{11} fraction) was passed through the established catalyst bed at a rate (WHSV) of 0.25 kg/l·h and was transferred outward at a rate of between 24 and 28 g/h. Reaction temperature or duration of the test were varied in the individual tests.

The following Table 1 shows the test conditions for the five tests and the thus obtained results.

Table 1
Process conditions and results for the solid bed method

Reaction conditions						
Temperature °C	100	120	140	160	160	
Pressure [bar]	20	20	20	25	25	
Operating hours	12	19	36	60	107	C_{12}-distillate
Liquid discharge [g/h]	24	27	27	28	27	
Composition in percent by weight						
C_6	68.5	52.7	43.6	57.0	73.2	0.1
$C_7 - C_{11}$	0.2	0.2	0.3	0.2	0.2	-
C_{12}	25.9	38.6	44.0	35.6	23.6	99.9
$> C_{12}$	5.4	8.5	12.1	7.2	3.0	-
Reaction rate	31.4	47.2	56.4	42.9	26.7	-

C_{12}-selectivity [% by weight]	82.5	81.8	78.2	83.0	88.4	-
S-content in the liquid discharge [ppm]	-	-	-	-	-	-

The product that was transferred outward was fractionated, distilled and the support structure isomers of the C_{12}-fraction was determined. The analysis yielded 14.2% by weight dodecene, 31.8% by weight 5-methyl undecene, 29.1% by weight 4-ethyl decene, 6.6% by weight 5,6-dimethyl decene, 9.3% by weight 4-methyl-5-ethyl nonene and 3.7% by weight diethyl octene.

B. Suspension method (fluidized bed)

A reactor that has a diameter of 20 mm, can be heated in an isothermal manner and has a volume of 157 ml was filled with 30 g of a catalyst with the composition indicated below:

50% by weight NiO, 34% by weight SiO_2, 13% by weight TiO_2, 3% by weight Al_2O_3 (according to DE-A-43 39 713), then conditioned for 24 hours in N_2 at 160 °C and used as a spray of between 0.05 and 0.5 mm.

The number of tests was 6, in which case 3-hexene (99.9% by weight, 0.1% by weight C_7 to C_{11} fraction) was passed from below through the fluidized bed catalyst at a rate of 0.25 kg/l·h. Most of the reaction product exiting the reactor was returned (return: feed quantity varied between approx. 45 and 60). Reaction temperature, feed quantity, circulation flow, return and the WHSV of the test were varied for the individual tests. The test lasted 8 hours.

The following Tables 2A and 2B show the test conditions for the six tests and the thus obtained results.

Table 2

Test conditions and results for the suspension method.

Table 2A
Process conditions

Test No.	Temperature [°C]	Pressure [bar]	Feed [g/h]	Circulation rate [g/h]	Return flow rate [X:1]	WHSV	Operating duration [h]
1	130	11.0	20	1200	60.0	0.127	8
2	130	11.0	23	1200	52.2	0.146	8
3	130	12.0	21	1100	52.4	0.134	8
4	130	12.2	24	1100	45.8	0.153	8
5	140	13.4	23	1180	51.3	0.146	8
6	150	14.1	22	1200	54.5	0.140	8

Table 2B
Composition of the reaction discharge

Test No.	% C_6	% > C_6	% C_{12}	% C_{18}	% C_{24}	% reaction rate	% C_{12}-selectivity
1	83.9	0.5	14.3	1.1	0.2	16.1	88.82
2	80.5	0.5	16.9	1.8	0.3	19.5	86.67
3	80.3	0.4	17.0	1.9	0.3	19.7	86.29
4	81.6	0.5	15.5	2.0	0.3	18.4	84.24
5	75.9	0.5	20.4	2.6	0.5	24.1	84.65
6	71.1	0.6	24.0	3.5	0.7	28.9	83.04

The product that was transferred outward was fractionated, distilled and the support structure isomers of the C_{12}-fraction were determined. The analysis yielded 14% by weight n-dodecene, 32% by weight 5-methyl undecene, 29% by weight 4-ethyl decene, 7% by weight 5,6-dimethyl decene, 9% by weight 4-methyl-5-ethyl nonene and 4% by weight diethyl octene.

Example 3

Hydroformylation of the dodecene mixture in accordance with the invention

A quantity of 750 g of the dodecene mixture produced according to example 2B was hydroformylated for 5 hours with 3.0 g $Co_2(CO)_8$ at 185 °C and at 280 bar CO/H_2 (volume ratio = 1 : 1.5) while adding 75 g H_2O in a lifting stirrer autoclave with a capacity of 2.5 liters. The reaction discharge was de-cobalted in an oxidative manner with 10% by weight acetic acid at 90 °C and with the introduction of air. While adding 10% by weight water, the oxo-product was hydrated for 10 hours in a 2.5 l lifting stirrer autoclave 50g Raney-Nickel at 125 W and 280 bar hydrogen pressure. The reaction discharge was distilled in a fractionated manner. A quantity of 450 g of a tri-decanol fraction produced in that manner was post-hydrated with 3.5 g $NaBH_4$.

The OH-number of the obtained tri-decanol was 277 KOH/g . The ^{1}H-NMR-spectroscopy

established an average branching degree of 2.3 methyl groups/molecule, corresponding to a branching degree of 1.3.

Examples 4A and 4B

Production of fatty alcohol ethoxylates

A. Fatty alcohol ethoxylates with 7 mol ethylene oxide

A quantity of 400 g of the alkanol mixture produced in accordance with example 3 were filled into a dry 2 l autoclave with 1.5 g NaOH. The autoclave content was heated to 150 °C and 616 g ethylene oxide was filled under pressure into the autoclave. After the whole ethylene oxide quantity had been filled in the autoclave, the autoclave was maintained at 150 °C for 30 minutes. The catalyst was neutralized by adding sulfuric acid after the cooling phase.

The thus obtained oxethylate represents a neutral tenside. It had a cloud point of 72 W, measured according to DIN 53917, 1% by weight in 10% by weight of an aqueous butyl di-glycol solution. The surface tension of a solution of 1 g/l of the substance in water was 27.3 mN/m, measured according to DIN 53914.

B. Fatty alcohol ethoxylates with 3 mol ethylene oxide

A quantity of 600 g of the alkanol mixture produced in accordance with example 3B was filled with 1.5 g NaOH into a dry autoclave with a capacity of 2 liters. The autoclave content was heated to 150 °C and 396 g ethylene oxide was placed under pressure into the autoclave. After the whole ethylene oxide quantity had been filled in the autoclave, the autoclave was maintained at 150 °C for 30 minutes. The catalyst was neutralized by adding sulfuric acid after the cooling phase.

The thus obtained oxethylate represents a neutral tenside. It had a cloud point of 43.5 °C, measured according to DIN 53917, 1% by weight in 10% by weight of an aqueous butyl di-glycol solution. The surface tension of a solution of 1 g/l of the substance in water was 26.1 mN/m, measured according to DIN 53914.

Examples 5A and 5B

Production of alkyl and alkyl ether phosphates

A. Alkyl phosphate

A quantity of 300 g of the alcohol mixture produced in accordance with example 3B was heated in a stirrer tank to 60 °C under nitrogen and was reacted slowly with 125 g poly-phosphoric acid. In that regard, the temperature shall not exceed 65 °C. Toward the end of the adding phase, the mixture was heated to 70 °C and was stirred further for one hour at this temperature.

The thus obtained product represents an anionic tenside. At a concentration of 1 g/l, an aqueous solution of the substance in water exhibited a surface tension of 29.8 mN/m, measured

according to DIN 53914.

B. Alkyl ether phosphate

A quantity of 560 g of the fatty alcohol oxethylate mixture produced in accordance with example 4B was heated to 60 °C in a stirrer tank under nitrogen and was reacted slowly with 92 g poly-phosphoric acid. In that regard, the temperature shall not exceed 65 °C. Toward the end of the adding phase, the mixture was heated to 70 °C and was stirred further for one hour at this temperature. The thus obtained product represents an anionic tenside. At a concentration of 1 g/l, an aqueous solution of the substance in water exhibited a surface tension of 37.7 mN/m, measured according to DIN 53914.

Patent claims

1. A method for the production of tenside alcohols and tenside alcohol ethers by way of a derivation of olefins with between approx. 10 and 20 C-atoms or of mixtures of such olefins and possibly a later alkoxylation, **characterized by the fact** that
    a)   a C_4-olefin mixture is exposed to a metathesis,
    b)   olefins with between 5 and 8 C-atoms are separated from the metathesis mixture,
    c)   the separated olefins are individually or in a mixture exposed to a dimerization to form olefin mixtures with between 10 and 16 C-atoms,
    d)   the thus obtained olefin mixture is - possibly after a fractionation - exposed to a derivatization to form a mixture of tenside alcohols and
    e)   the tenside alcohols are possibly alkoxylated.

2. A method in accordance with claim 1, characterized by the fact that process step a) - the metathesis - is performed in the presence of catalysts that contain molybdenum, tungsten or rhenium catalysts.

3. A method in accordance with at least one of claims 1 and 2, characterized by the fact that one separates the olefins with 5 and 6 C-atoms in process step b).

4. A method in accordance with at least one of claims 1 through 3, characterized by the fact that process step c) - the dimerization - is performed in a heterogeneous manner.

5. A method in accordance with at least one of claims 1 through 4, characterized by the fact that one uses a dimerization catalyst containing at least one element from secondary group VIII of the periodic system, and that the catalyst composition and the reaction conditions are selected such that one obtains a dimer mixture that contains less than 10% by weight of compounds containing a structural element of the formula I (vinyl idene group)
/formula/
where A^1 and A^2 are aliphatic hydrocarbon rests.

6. A method in accordance with at least one of claims 1 through 5, characterized by the fact that the olefins with 5 and 6 C-atoms are dimerized individually or in a mixture in process step c).

7. A method in accordance with at least one of claims 1 through 6, characterized by the fact that the 3-hexene is dimerized in process step c).

8. A method in accordance with at least one of claims 1 through 7, characterized by the fact that the derivation (process step d)) is performed by way of a hydroformylation.

9.   The new olefin mixtures that can be produced according to the process steps a), b) and c) of the method indicated in claim 1.

10.   Olefin mixtures in accordance with claim 9, characterized by the fact that they have a percentage content of linear olefins of less than 25% by weight and preferably of less than 20% by weight.

11.   Olefin mixtures in accordance with at least one of claims 9 and 10, characterized by the fact that at least 80% of the components of the dimerization mixture have one branching or two branchings at adjacent C-atoms at an area located at 1/4 to 3/4 and preferably at 1/3 to 2/3 of the chain length of their main chain.

12.   Olefin mixtures in accordance with at least one of claims 9 through 11, characterized by the fact that mainly groups with (y-4) and (y-5) C-atoms are linked at the branching points of the main chain, in which case y is the number of carbon atoms in the monomer used for the dimerization.

13.   Olefin mixtures in accordance with at least one of claims 9 through 12, characterized by the fact that the ratio between aliphatic and olefinic hydrogen atoms varies over a range of

$H_{aliphatic} : H_{olefinic} = (2 \times n\text{-}0.5) : 0.5$ to $(2 \times n\text{-}1.9) : 1.9$, where n

represents the carbon atom number of the olefin obtained with the dimerization.

14.   Olefin mixtures in accordance with at least one of claims 9 through 13, characterized by the fact that the ratio between aliphatic and olefinic hydrocarbon atoms varies over a range of $H_{aliphatic} : H_{olefinic} = (2 \times n\text{-}1.0) : 1$ to $(2 \times n\text{-}1.6) : 1.6$.

15.   The new tenside alcohols and their alkoxylation products that can be produced according to process steps a), b), c), d) and possibly e) of the method indicated in claim 1.

16.   The use of the tenside alcohol alkoxylation products in accordance with claim 15 as non-ionic tensides.

17.   The use of the tenside alcohols in accordance with claim 15 for the production of tensides.

18.   The use of the tenside alcohols in accordance with claim 15 for the production of alkanol glycoside and poly-glycoside mixtures through a single or multiple reaction (glycosidation) with mono-, di- or poly-saccharides with the exclusion of water under an acid catalyst or with O-acetyl saccharide halides.

19.   The use of the tenside alcohols and their alkoxylation products in accordance with claim 15 for the production of surface-active sulfates by esterifying them with sulfuric acid or derivatives of sulfuric acid to form acid alkyl sulfates or alkyl ether sulfates.

20.   The use of the tenside alcohols and their alkoxylation products in accordance with claim 15 for the production of surface-active phosphates by esterifying them with phosphoric acid or its derivatives to form alkyl phosphates or alkyl ether phosphates.